Abstract

Conventional PU products usually prepared from petroleum derived polyols contain significant amount of organic solvents. Environmental concerns regarding volatile organic compounds (VOC) and hazardous air pollutants (HAPs), limited fossil resources and economic competitiveness have motivated academic and industrial researchers towards the enhanced use of renewable feedstock for the production of eco-friendly polyurethane materials. Thrust is more on vegetable oil based waterborne polyurethane dispersions (PUDs) due to their environmental friendly nature, low viscosity at high molecular weight, reduced material costs associated with organic solvent and good applicability in many fields especially as coatings and adhesives for automobiles, wood, leathers and textiles. However, all these PUDs contain dimethylol propionic acid (DMPA) as internal emulsifier, which leads to low phase compatibility between hard and soft segments and high film formation time. In addition, the resulting PUD coatings suffer from poor surface properties.

The aim of this thesis was to develop new DMPA free waterborne PU dispersions and its copolymer dispersions from cotton seed oil based ionizable polyols i.e. polyols which have both OH groups and ionizable groups for coating applications. The study includes synthesis of the ionizable polyols, their characterization and their utilization in developing waterborne anionic PUDs. The characterization of PUDs and their cured films using different techniques have also been carried out. In addition, the coating properties of the PUDs have also been investigated.

Maleated hydroxylated polyol, an ionizable polyol (MAHCSO) was synthesized by maleanization of hydroxylated cottonseed oil polyol (HCSO). This maleated polyol (MAHCSO) was employed to develop anionic waterborne PUDs through a prepolymer method. The prepolymer was synthesized from MAHCSO, IPDI and hexane diol and neutralized with different counter cations and dispersed in water, subsequently chain extended with different aliphatic dihydrazides. Three different series of PUDs have been developed by varying the (i) ionic content (ii) chain extender and (iii) countercation. The significant effect of the ionic content of the polyol (MAHCSO), chain length of dihydrazides and hydroxy alkyl chains of countercation on particle size distributions, zeta potential distributions and viscosities of final PUDs and physico-chemical, thermo-mechanical and coating properties of the cured PUD films were observed. It was observed that PUD-ADH with TEA countercation and ionic content of 0.5

equiv. exhibited good storage stability, water contact angle, T_g and mechanical strength as well as coating properties.

As a next step, a series of novel, DMPA free, catalyst free, anionic waterborne polyurethane-imide (PUID) dispersions have been successfully synthesized by using above mentioned maleated cottonseed oil polyol (MAHCSO) as an ionic soft segment, TDI as isocyanate and dianhydride as chain extenders. Three different aromatic dianhydrides were employed as chain extenders to introduce the imide functionality in the polyurethane hard segment and their effect on thermo-mechanical properties and phase compatibility between hard and soft segments were investigated. The cured films were characterized by different techniques including FT-IR (ATR), TGA, DMTA, UTM, and contact angle measurements. It was found that the tensile properties, thermal stability, water contact angle, and T_g values of PUIDs were remarkably high compared to neat PUD.

In an attempt to introduce other ionic groups in the poyol, phosphorylated polyols (phospol-P5, P10 and P15) bearing both hydroxyl and ionizable phosphoryl groups were synthesized through the ring opening hydrolysis of epoxy cottonseed oil (ECSO) with different concentrations of *ortho* phosphoric acid. Three different phosphols were synthesized and used for the development of a novel class of DMPA free and catalyst free anionic waterborne PUDs through a sol-gel technique using IPDI and 3-aminopropyl triethoxysilane (APTES). The obtained phospols were characterized by ^{1}H NMR, FTIR, hydroxyl value, acid value, gel permentation chromatography (GPC) and rheological studies. The synthesized PUDs and their cured films were characterized by different techniques including zeta sizer, FTIR (ATR), Solid state ^{29}Si NMR, TGA, DMTA, DSC, and UTM. The hydrophobic nature of the films was measured by contact angle technique and their anti corrosion performance was studied through polarization technique. The films of PUD-P5 exhibited the highest tensile strength, thermal stability, T_g, contact angle and good anticorrosive properties due to the high degree of siloxane crosslinking.

In the next approach, an ionizable polyol was synthesized by ring opening of epoxidized cottonseed oil (ECSO) with 4-aminobenzoic acid (PABA) and blended with hydroxylated cottonseed oil polyol (HCSO) in different weight ratios to give mixed polyols having different hydroxyl numbers viz., 131, 118 and 106 mg KOH/g. Three different PUDs were synthesized using the mixed polyols, IPDI and 3-aminopropyltriethoxysilane. The chemical structure, thermo-mechanical properties and surface properties of cured PUD films were examined using FTIR, TGA, DMTA and contact angle measurements. The effect of Si─O─Si cross-linking density, which increases with increasing OH values of the mixed polyol, was also investigated. All the PUDs prepared in this study exhibited good storage stability (> 4 months), and the average particle sizes of PUDs ranged from 18 to 124 nm. The PUD film (PUD-35 film) prepared with mixed polyol having the highest hydroxyl value exhibited high thermal stability, mechanical strength; T_g, water contact angle value, chemical, abrasion and scratch resistance due to the extensive siloxane cross-links.

List of Schemes

List of Figures

List of Tables

List of Abbreviations

ADH	Adipic dihydrazide
APTES	Aminopropyl triethoxysilane
AV	Acid value
E_{ac}	Activation energy
BPOTCDA	Benzophenone-tetracaroboxylic dianhydride
CHDM	Cyclohexane-1,6-dimethylol
Ecorr	Corrosion potential
Icorr	Corrosion current
DMEA	Dimethylethanolane
DHZ	Dihydrazide
DMPA	Dimethylol propanoic acid
DMF	Dimethylformamide
DMTA	Dynamic mechanical and thermal analysis
DSC	Differential scanning calorimetry
DTG	Derivative thermogram
ECSO	Epoxidized cottonseed oil
EA	Ethyl acetate
ε	Elongation at break
FA	Formic acid
FT-IR	Fourier transform infrared
g	Grams
GPC	Gel permeation chromatography
T_g	Glass transition temperature
HCSO	Hydroxylated cottonseed oil
HDO	Hexane 1,6-diol
HFIPDA	Hexafluoroisopropylidine-dipthalic anhydride
HV	Hydroxyl value
HSC	Hard segment content
IPDI	Isophorone diisocyanate
MAHCSO	Maleated hydroxylated Cottonseed oil

MA	Maleic anhydride
MEK	Methyl ethyl ketone
mg	Milligram
MS	Mild steel
MHz	Megahertz
mL	Millilitre
MPa	Megapascal
NMDA	*N*-Methyl diethanolamine
NMR	Nuclear magnetic resonance
N	Normality
nm	Nano meter
M_n	Number average molecular weight
ODH	Oxalic dihydrazide
OOC	Oxirane oxygen content
Phospol	Phosphorylated polyol
PABA	Para-aminobenzoic acid
PMDA	Pyromellitic dianhydride
PU	Polyurethane
PUD	Polyurethane dispersion
PUID	Polyurethane-imide dispersion
PDI	Polydispersity index
SDH	Succinic dihydrazide
SBDH	Sebacic dihydrazide
E'	Storage modulus
TEA	Tri ethyl amine
TEOA	Triethanolamine
TDI	Toluene diisocyanate
TGA	Thermo gravimetric analysis
σ	Tensile strength
UTM	Universal testing machine
M_w	Weight average molecular weight
E	Young's modulus